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# Synthesis and NMR spectra of the tryptophan-containing derivatives of deuteroporphyrin IX

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**Deuteroporphyrin IX derivatives containing tryptophan and quinone residues were synthesised and intramolecular interactions between the nitrogen atoms of the porphyrin ring and the NH group of the indole ring of tryptophan were detected in these compounds.**

The development of new artificial photocatalytic systems and molecular photonic and electronic devices[1] for the conversion of sunlight energy into the energy of chemical bonds is based on the principles of naturally occurring photosynthesis. Porphyrins and their derivatives, which are similar to chlorines in many structural, chemical and photochemical characteristics, are the main components of these systems. It is well known[2,3] that aromatic amino acids participate in the formation of optimum conditions for the process of primary photosynthetic charge separation. However, among the described artificial photoconverting systems, only a few structures containing amino acid residues or peptide fragments are known.[4–6]

We synthesised compounds **1** and **2** containing 2,7,12,18-tetramethyl-13,17-bis(2-carboxyethyl)porphine (deuteroporphyrin IX) and tryptophan (Trp). Ditryptophan derivative **1** was synthesised from deuteroporphyrin **3** by the method of mixed anhydrides with the use of di-*tert*-butyl dicarbonate ($Boc_2O$) as an activating agent in the presence of pyridine and *N*,*N*-dimethylaminopyridine (DMAP).[7,8] Derivative **2** was prepared analogously from the monomethyl ester of deuteroporphyrin IX (**4**). Note that compound **2** was isolated as a mixture of two isomers at the 13- and 17-positions of the porphyrin macrocyclic ring because they could not be separated by chromatography.

Because quinones play the role of electron acceptors in natural photosystems, we synthesised ternary systems containing an aromatic amino acid residue, a porphyrin and a quinone component. The strategy of the synthesis of compound **5** was based on the results of our previous studies.[9] The synthesis was performed in two steps by the replacement of an OH group in the molecule of deuteroporphyrin **3** by a 2-(2-hydroxyethyl)-thio-3-methyl-1,4-naphthoquinone residue with the formation of monoquinone derivative **6** (as a mixture of two isomers) followed by the introduction of the methyl ester of tryptophan at the free COOH group. Monoquinone derivative **6** was prepared by the method of mixed anhydrides with the use of pivaloyl chloride as an activating agent.[10] The introduction of the tryptophan residue was performed as in the syntheses of derivatives **1** and **2**.

The structures of compounds **1**, **2** and **5** were supported by UV-VIS, IR and NMR spectroscopy, mass spectrometry and elemental analysis.‡

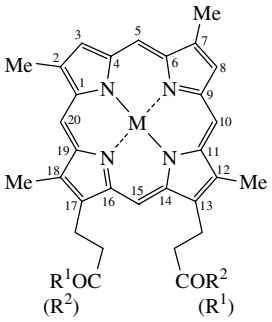
The upfield shifts of the aromatic protons signals of Trp residues (by ~0.5–1.8 ppm) and quinone (by ~0.5 ppm) in the

† Deceased.

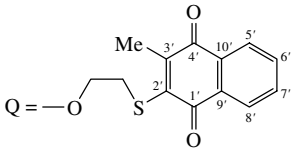
**Table 1** $^1$H NMR chemical shifts of the Trp and quinone parts.

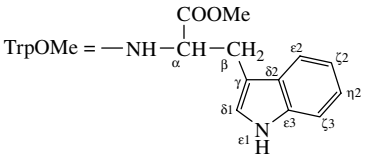
| Group | Proton | δ/ppm for compounds | | | | |
|---|---|---|---|---|---|---|
| | | Boc-TrpOH | **2** | **8** | **5** | **9** |
| Trp | NH amide | | 5.68 | 6.30 | 5.94, 5.92 | 6.85, 6.83 |
| | $C^{\alpha}H$ | 4.67 | 4.25 | 4.74 | 4.42 | 4.93, 4.94 |
| | $C^{\beta}H_2$ | 3.36 | 2.49 | 2.77, 2.83 | 2.59 | 3.10 |
| | $C^{\delta1}H$ | 7.05 | broad | 5.42, 5.45 | broad | 5.93 |
| | NH | 8.75 | broad | 6.75, 6.79 | broad | 7.09 |
| | $C^{\varepsilon2}H$ | 7.62 | 6.80, 6.82 | 7.08, 7.09 | 6.88 | 7.24 |
| | $C^{\zeta2}H$ | 7.14 | 6.53 | 6.73 | 6.54 | 6.79 |
| | $C^{\zeta3}H$ | 7.36 | 6.53 | 6.73 | 6.54 | 6.79 |
| | $C^{\eta2}H$ | 7.22 | 5.43, 5.48 | 6.54 | 5.60 | 6.62 |
| Quinone | 3′-Me | | | | 1.45, 1.55 | 0.70, 0.77 |
| | $C^{5'}H$ | | | | 7.66, 7.68 | 6.80 |
| | $C^{6'}H$ | | | | 7.30 | 7.25 |
| | $C^{7'}H$ | | | | 7.32 | 7.10 |
| | $C^{8'}H$ | | | | 7.54, 7.55 | 6.40, 6.39 |
| | –S–$CH_2$– | | | | 2.67 | 1.62, 1.71 |
| | –$CH_2$–O– | | | | 3.78, 3.92 | 3.06, 3.20 |

$^1$H NMR spectra of compounds **1**, **2** and **5** are due to an effect of the magnetic anisotropy of the porphyrin ring (Table 1). They indicate that these fragments are arranged above and below the porphyrin plane in its diamagnetic region (within a cone with the axis perpendicular to the plane of the porphyrin ring). The shifts of the signals are typical of structures with a flexible covalent bridge between chromophores and related to their conformational dynamics in solution.[10,11]



**1** M = 2H, $R^1 = R^2$ = TrpOMe
**2** M = 2H, $R^1$ = OMe, $R^2$ = TrpOMe
**3** M = 2H, $R^1 = R^2$ = OH
**4** M = 2H, $R^1$ = OH, $R^2$ = OMe
**5** M = 2H, $R^1$ = Q, $R^2$ = TrpOMe
**6** M = 2H, $R^1$ = Q, $R^2$ = OH
**7** M = Zn, $R^1 = R^2$ = TrpOMe
**8** M = Zn, $R^1$ = OMe, $R^2$ = TrpOMe
**9** M = Zn, $R^1$ = Q, $R^2$ = TrpOMe





We failed to detect signals due to protons at the $C^{\delta1}$ and $N^{\varepsilon1}$ atoms of the Trp indole ring in the $^1$H NMR spectra of compounds **1**, **2** and **5** [Figure 1(*a*) shows a fragment of the $^1$H NMR spectrum of compound **2**]. Cross peaks between protons at the $C^{\beta}$ and $C^{\delta1}$ atoms are absent from the TOCSY spectra. However, the signals of molecular ions in the mass spectra of these compounds and elemental analysis data suggest that the indole ring remained undegraded in the course of reactions and isolation; consequently, the structures of the resulting derivatives correspond to formulas **1**, **2** and **5**. The cross peak of the $C^{\delta1}$ atom and its proton was absent from the $^1$H–$^{13}$C HMQC correlation spectrum. However, the $^1$H–$^{13}$C HMBC spectrum suggests the presence of the $C^{\delta1}$ atom, whose chemical shift (121.49 ppm) is indicative of the retention of the indole ring structure (the chemical shift of the same carbon in free tryptophan is 119.50 ppm).

It is evident that the signals of protons at the $C^{\delta1}$ and $N^{\varepsilon1}$ atoms cannot be detected in the $^1$H NMR spectra because of a strong broadening due to conformation exchange in solution; the rate of this exchange is comparable to the time scale of NMR spectroscopy. This also explains the broadening of signals due to the other protons of the indole ring of tryptophan, which was observed in the $^1$H NMR spectra.

To explain the observed diamagnetic shift of signals due to the aromatic protons of Trp residues, we hypothesised that a flexible covalent bridge between the porphyrin and the amino acid residue allows the indole ring of Trp to approach the centre of the porphyrin plane. In the conformation characterised by a minimally possible distance between porphyrin and Trp moieties, the nitrogen atoms of the porphyrin ring interact with the NH group of the indole ring of Trp. Because $C^{\delta1}$ is close to the NH group of the indole, the hydrogen atom at it is also strongly affected by the magnetic anisotropy of porphyrin. On the other hand, the absence of cross peaks between the protons of the six-membered ring of the amino acid residue and the porphyrin macrocycle from the NOESY spectra suggests that the distance between them is longer than 5 Å. It is most likely that the indole ring comes nearer to the porphyrin plane and is arranged at an angle; in this case, the six-membered aromatic ring is distant from the porphyrin plane and the heterocyclic ring is close to it.§ However, the flexibility of the covalent bridge results in the occurrence of a number of other confor-

‡ The UV-VIS spectra of compounds **1**, **2** and **5** retained the type and positions of absorption band maximums corresponding to the dimethyl ester of deuteroporphyrin IX.

The NMR spectra were measured on a Bruker Avance DRX-500 instrument in $CDCl_3$ (500 and 125 MHz for $^1$H and $^{13}$C, respectively). Chemical shifts were measured with reference to the residual signal of $CDCl_3$ ($\delta$ 7.27 ppm).

**2**: yield 71%. $^1$H NMR, $\delta$: 2.49 (m, 4H, $2C^{\beta}H_2$), 3.10 (m, 2H, $CH_2CON$), 3.21 (m, 2H, $CH_2COO$), 3.23 (m, 2H, $CH_2CON$), 3.34 (m, 2H, $CH_2COO$), 3.38 (s, 6H), 3.47 (s, 3H), 3.48 (s, 3H, 4COOMe), 3.58 (s, 3H, 12-Me), 3.60 (s, 3H, 18-Me), 3.62 (s, 3H, 12-Me), 3.64 (s, 3H, 18-Me), 3.74 (s, 3H, 2-Me), 3.77 (s, 3H, 7-Me), 3.80 (s, 6H, 2-Me, 7-Me), 4.25 (m, 2H, $2C^{\alpha}H$), 4.34 (m, 2H, $CH_2CH_2COO$), 4.36 (m, 2H, $CH_2CH_2CON$), 4.40 (m, 2H, $CH_2CH_2COO$), 4.56 (m, 2H, $CH_2CH_2CON$), 5.43 (m, 1H), 5.48 (m, 1H, $2C^{\eta2}H$), 5.68 (m, 2H, 2CONH), 6.53 (m, 4H, $2C^{\zeta2}H$, $2C^{\zeta3}H$), 6.80 (m, 1H), 6.82 (m, 1H, $2C^{\varepsilon2}H$), 9.10 (s, 1H, $C^8H$), 9.16 (s, 2H, $C^8H$, $C^3H$), 9.18 (s, 1H, $C^3H$), 10.00 (s, 1H), 10.08 (s, 1H, $2C^{10}H$), 10.09 (s, 1H, $C^{20}H$), 10.16 (s, 2H, $C^5H$, $C^{20}H$), 10.17 (s, 3H, $C^5H$, $2C^{15}H$). IR, $\nu$/cm$^{-1}$: 3333 (NH), 1726 (C=O ester), 1650 (amide I), 1526 (amide II). MS, *m*/*z*: 725 $[M + H]^+$.

**5**: yield 21%. $^1$H NMR, $\delta$: 1.45 (s, 3H), 1.55 (s, 3H, 2×3′-Me), 2.59 (m, 4H, $2C^{\beta}H_2$), 2.67 (m, 4H, $2SCH_2CH_2O$), 3.09 (m, 2H), 3.12 (m, 2H, $2CH_2COO$), 3.14 (m, 2H), 3.24 (m, 2H, $2CH_2CON$), 3.49 (s, 3H), 3.50 (s, 3H, 2COOMe), 3.56 (s, 9H, 2×12-Me, 18-Me), 3.58 (s, 3H, 18-Me), 3.70 (s, 3H, 2-Me), 3.75 (s, 3H, 7-Me), 3.76 (s, 3H, 7-Me), 3.77 (s, 3H, 2-Me), 3.78 (m, 2H), 3.92 (m, 2H, $2SCH_2CH_2O$), 4.25 (m, 2H, $CH_2CH_2COO$), 4.31 (m, 2H, $CH_2CH_2CON$), 4.33 (m, 2H, $CH_2CH_2COO$), 4.42 (m, 2H, $2C^{\alpha}H$), 4.52 (m, 2H, $CH_2CH_2CON$), 5.60 (m, 2H, $2C^{\eta2}H$), 5.92 (m, 1H), 5.94 (m, 1H, 2CONH), 6.54 (m, 4H, $2C^{\zeta2}H$, $2C^{\zeta3}H$), 6.88 (m, 2H, $2C^{\varepsilon2}H$), 7.30 (m, 2H, $2C^{6'}H$), 7.32 (m, 2H, $2C^{7'}H$), 7.54 (m, 1H), 7.55 (m, 1H, $2C^{8'}H$), 7.66 (m, 1H), 7.68 (m, 1H, $2C^{5'}H$), 9.04 (s, 1H, $C^8H$), 9.10 (s, 1H, $C^3H$), 9.11 (s, 1H, $C^8H$), 9.13 (s, 1H, $C^3H$), 9.92 (s, 1H, $C^{10}H$), 9.97 (s, 1H, $C^{20}H$), 10.02 (s, 1H, $C^{10}H$), 10.07 (s, 1H, $C^{15}H$), 10.08 (s, 3H, $2C^5H$, $C^{15}H$), 10.12 (s, 1H, $C^{20}H$). $^{13}$C NMR, $\delta$: 12.19 (12-Me, 18-Me), 14.14 (2-Me), 14.21 (2-Me, 7-Me), 14.86 (3′-Me), 22.19 ($CH_2CH_2COO$), 23.35 ($CH_2CH_2CON$), 27.26 ($C^{\beta}$), 32.70 ($SCH_2$), 36.85 ($CH_2COO$), 40.03 ($CH_2CON$), 52.81 ($C^{\alpha}$, OMe), 64.49, 64.54 ($SCH_2CH_2O$), 97.68 ($C^{15}$), 97.84, 98.12 ($C^{20}$), 100.06, 100.42 ($C^{10}$), 101.04 ($C^5$, $C^{15}$), 108.34 ($C^{\gamma}$), 110.74 ($C^{\eta2}$), 117.88 ($C^{\varepsilon2}$), 118.94 ($C^{\zeta3}$), 121.37 ($C^{\zeta2}$), 121.49 ($C^{\delta1}$), 126.62 ($C^{5'}$), 126.64 ($C^{8'}$), 126.74 ($C^{\delta2}$), 129.05 ($C^3$, $C^8$), 129.91 ($C^8$), 131.90 ($C^{9'}$), 133.39 ($C^{10'}$), 133.60 ($C^{6'}$, $C^{7'}$), 134.84 ($C^{\varepsilon3}$), 137.25 ($C^{12}$), 137.92 ($C^{18}$), 139.03 ($C^{13}$), 139.44 ($C^{17}$), 140.51 ($C^2$), 141.63 ($C^7$), 145.33, 145.60 ($C^{2'}$), 146.39, 146.52 ($C^{3'}$), 172.78 (COO Trp), 173.39 (CON), 173.59 ($COO\text{-}CH_2$), 180.59, 180.75 ($C^{1'}$), 181.62, 181.76 ($C^{4'}$). IR, $\nu$/cm$^{-1}$: 3302 (NH), 1733 (C=O ester), 1655 (C=O quinone, amide I), 1523 (amide II). MS, *m*/*z*: 941 $[M + H]^+$.

§ The molecular geometry of compound **5** was obtained by computer simulation using the MM+ method (Autodesk HyperChem program, versions 2.0 and 3.0).

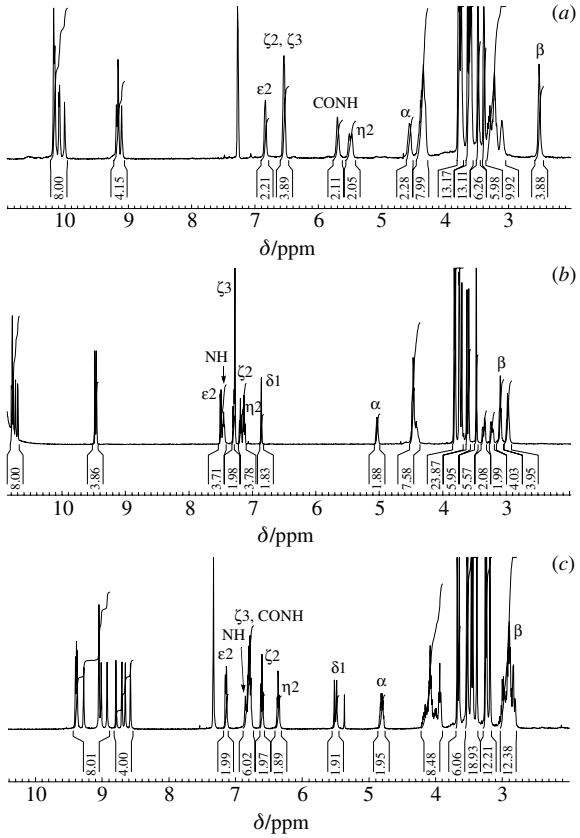



**Figure 1** $^1$H NMR spectra of compounds (*a*) **2**, (*b*) **2** ($CDCl_3$ + 5% $CF_3COOH$) and (*c*) **8**, 30 °C.

mations with the larger separations between the indole ring of tryptophan and the porphyrin plane.

A strong dilution of the test solution (by a factor of ~50) did not result in changes in the $^1$H NMR spectrum (the signals of protons at the $C^{\delta1}$ and $N^{\varepsilon1}$ atoms of the indole ring were not detected). Evidently, this suggests an intramolecular character of interactions between the indole ring of the amino acid fragment and the porphyrin macrocycle.

The addition of 5 vol.% trifluoroacetic acid to solutions of compounds **1** and **2** in $CDCl_3$ resulted in the appearance of two signals due to protons at the $C^{\delta1}$ and $N^{\varepsilon1}$ atoms in the $^1$H NMR spectra [Figure 1(*b*)]. Moreover, the signals of the other protons of the Trp residue shifted downfield by 0.5–1.4 ppm and became better resolved (narrowed). Thus, the protonation of nitrogen atoms of the porphyrin macrocycle resulted in the disappearance of its interaction with the indole ring of the amino acid fragment.

A similar effect of the disappearance of intramolecular interactions was observed in compounds **7**, **8** and **9**¶ when introducing a Zn atom into the porphyrin macrocycle [Figure 1(*c*)]. The $^1$H NMR spectra of compounds **7**, **8** and **9** also exhibited signals due to protons at the $C^{\delta1}$ and $N^{\varepsilon1}$ atoms, whereas the signals of the protons of the six-membered aromatic ring shifted downfield by ~0.2–1 ppm. This is indicative of the removal of the indole ring of tryptophan from the porphyrin plane upon the introduction of the zinc atom. Note that no coordination of the zinc atom with the indole ring of tryptophan as an axial ligand was observed in zinc complexes **7**, **8** and **9**. This follows from the absence of the absorption bands shifts in the UV-VIS spectra of the deuteroporphyrin zinc complex. The signals of aromatic protons of the quinone fragment in the $^1$H NMR spectrum of triad **9** were shifted upfield with respect to the corresponding signals in metal-free compound **5**. Consequently, the introduction of the metal atom resulted in a change in the mutual arrangement of three aromatic systems in the triad and in the disappearance of the interaction between the porphyrin and tryptophan.

Thus, we synthesised compounds including deuteroporphyrin IX, tryptophan and quinone. Intramolecular interactions between the N atoms of the porphyrin and the $N^{\varepsilon1}H$ group of tryptophan were detected by NMR spectroscopy. The protonation or metalation of the porphyrin macrocycle resulted in the disappearance of these interactions.

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## References

1 A. K. Burrell and M. R. Wasielewski, *J. Porphyrins Phthalocyanines*, 2000, **4**, 401.
2 L. M. P. Beekman, I. H. M. van Stokkum, R. Monshouwer, A. J. Rijnders, P. McGlynn, R. W. Visschers, M. R. Jones and R. van Grondelle, *J. Phys. Chem.*, 1996, **100**, 7256.
3 H. A. Murchison, R. G. Alden, J. P. Allen, J. M. Peloquin, A. K. W. Taguchi, N. W. Woodbury and J. C. Williams, *Biochemistry*, 1993, **32**, 3498.
4 D. A. Williamson and B. E. Bowler, *J. Am. Chem. Soc*., 1998, **120**, 10902.
5 M. Ushiyama, A. Yoshino, T. Yamamura, Y. Shida and F. Arisaka, *Bull. Chem. Soc. Jpn*., 1999, **72**, 1351.
6 H. Tamiaki, S. Suzuki and K. Maruyama, *Bull. Chem. Soc. Jpn*., 1993, **66**, 2633.
7 V. F. Pozdnev, *Bioorg. Khim*., 1985, **11**, 725 (in Russian).
8 V. V. Borovkov, A. A. Gribkov, A. N. Kozyrev, A. S. Brandis, A. Ishida and Y. Sakata, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1533.
9 R. P. Evstigneeva, V. Z. Pashchenko, V. N. Luzgina, E. A. Larkina, A. A. Gribkov, V. B. Tusov and V. V. Gorokhov, *Dokl. Akad. Nauk*, 1999, **369**, 57 [*Dokl. Chem.* (*Engl. Transl.*), 1999, **369**, 261].
10 V. V. Borovkov, E. I. Filippovich and R. P. Evstigneeva, *Khim. Geterotsikl. Soedin*., 1988, 608 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1988, **24**, 494].
11 T. Hayashi, T. Takimura, Y. Hitomi, T. Ohara and H. Ogoshi, *J. Chem. Soc., Chem. Commun*., 1995, 545.

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¶ The introduction of the metal was monitored by UV–VIS spectroscopy detecting the disappearance of absorption bands at 496 and 618 nm and an increase in the molar extinction coefficients of the other bands.

**8**: $^1$H NMR, $\delta$: 2.77 (m, 2H, $C^{\beta}H_2$), 2.8 (m, 2H, $CH_2COO$), 2.83 (m, 2H, $C^{\beta}H_2$), 2.84 (m, 2H), 2.9 (m, 2H), 2.94 (m, 2H, $3CH_2COO$), 3.12 (s, 3H, 18-Me), 3.17 (s, 3H, COOMe), 3.19 (s, 6H, COOMe, 18-Me), 3.32 (s, 3H, 12-Me), 3.38 (s, 3H, 2-Me), 3.40 (s, 3H, 12-Me), 3.45 (s, 3H, COOMe), 3.47 (s, 6H, COOMe, 2-Me), 3.59 (s, 3H), 3.62 (s, 3H, 2×7-Me), 3.87 (m, 2H), 3.93 (m, 2H, $2CH_2CH_2COO$), 4.02 (m, 2H), 4.11 (m, 2H, $CH_2CH_2CON$), 4.74 (m, 2H, $2C^{\alpha}H$), 5.42 (m, 1H), 5.45 (m, 1H, $2C^{\delta1}H$), 6.30 (m, 2H, 2CONH), 6.54 (m, 2H, $2C^{\eta2}H$), 6.73 (m, 4H, $2C^{\zeta2}H$, $2C^{\zeta3}H$), 6.75 (m, 1H), 6.79 (m, 1H, $2C^{\delta1}H$–N*H*), 7.08 (m, 1H), 7.09 (m, 1H, $2C^{\varepsilon2}H$), 8.51 (s, 1H), 8.59 (s, 1H, $2C^{3}H$), 8.64 (s, 1H), 8.73 (s, 1H, $2C^{8}H$), 8.86 (s, 1H, $C^{20}H$), 8.96 (s, 1H, $C^{15}H$), 8.99 (s, 2H, $C^{15}H$, $C^{20}H$), 9.22 (s, 1H, $C^{10}H$), 9.31 (s, 1H, $C^{5}H$), 9.33 (s, 1H, $C^{10}H$), 9.34 (s, 1H, $C^{5}H$).

**9**: $^1$H NMR, $\delta$: 0.70 (s, 3H), 0.77 (s, 3H, 3′-Me), 1.62 (m, 2H), 1.71 (m, 2H, $2SCH_2CH_2O$), 2.89 (m, 2H), 2.93 (m, 2H, $2CH_2CON$), 3.06 (m, 4H, $CH_2COO$, $SCH_2CH_2O$), 3.08 (m, 2H, $CH_2COO$), 3.10 (m, 4H, $2C^{\beta}H_2$), 3.20 (m, 2H, $SCH_2CH_2O$), 3.38 (s, 3H), 3.43 (s, 3H, 2×18-Me), 3.46 (s, 3H), 3.50 (s, 3H, 2×12-Me), 3.54 (s, 6H, 2COOMe), 3.57 (s, 3H, 2-Me), 3.61 (s, 3H, 7-Me), 3.62 (s, 6H, 2-Me, 7-Me), 4.07 (m, 2H, $CH_2CH_2CON$), 4.18 (m, 2H, $CH_2CH_2COO$), 4.20 (m, 2H, $CH_2CH_2CON$), 4.23 (m, 2H, $CH_2CH_2COO$), 4.93 (m, 1H), 4.94 (m, 1H, $2C^{\alpha}H$), 5.93 (m, 2H, $2C^{\delta1}H$), 6.39 (m, 1H), 6.40 (m, 1H, $2C^{8'}H$), 6.62 (m, 2H, $2C^{\eta2}H$), 6.79 (m, 4H, $2C^{\zeta2}H$, $2C^{\zeta3}H$), 6.80 (m, 2H, $2C^{5'}H$), 6.83 (m, 1H), 6.85 (m, 2H, 2CONH), 7.09 (m, 2H, $2C^{\delta1}H$–N*H*), 7.10 (m, 2H, $2C^{7'}H$), 7.24 (m, 2H, $2C^{\varepsilon2}H$), 7.25 (m, 2H, $2C^{6'}H$), 8.80 (s, 2H, $C^{3}H$, $C^{8}H$), 8.85 (s, 1H, $C^{3}H$), 8.88 (s, 1H, $C^{8}H$), 9.47 (s, 1H, $C^{20}H$), 9.49 (s, 2H, $2C^{15}H$), 9.56 (s, 2H, $C^{5}H$, $C^{10}H$), 9.57 (s, 1H, $C^{5}H$), 9.60 (s, 1H, $C^{20}H$), 9.66 (s, 1H, $C^{10}H$).